

SHORT COMMUNICATION

KINETIC SPECTROPHOTOMETRIC DETERMINATION OF IRON BASED ON CATALYTIC OXIDATION OF *p*-ACETYLARSENAZO

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ABSTRACT. A novel catalytic kinetic spectrophotometric method for the determination of iron is developed based on the catalytic effect of Fe(III) on the oxidation reaction of *p*-acetylarsenazo(ASApA) by potassium periodate. Maximum absorbance of the Fe(III)-ASApA-KIO₄ system in 8.0×10^{-3} M sulfuric acid occurs at the wavelength of 540 nm. The change in absorbance (ΔA) is linearly related with the concentration of iron(III) in the range of 0.10-4.0 ng/mL and fitted the equation: $\Delta A = 4.91 \times 10^{-2} C$ (C: ng/mL) + 0.017, with a regression coefficient of 0.9966 at the wavelength. The detection limit of the method is 0.031 ng/mL. The relative standard deviation of the method was from 1.34% to 1.78% for 11 replicate determinations. The standard addition recovery of the method ranged from 95.71% to 103.3%. The method was used to determine iron in the black gingili paste, oat slice, sleeve-fish silk food samples. The determined results were in agreement with those by atomic absorption spectrometry.

KEY WORDS: Iron, Catalytic kinetic spectrophotometry, *p*-Acetylarsenazo, Potassium periodate

INTRODUCTION

Iron is an important component for the human body. It is not only necessary for the exchange and transportation of oxygen gas in the blood of a human body, but also is an indispensable element for some enzymes and many oxidation-reduction systems. It plays an important role in the aspect of biological catalysis, the transportation of electrons on breath chains, etc. A deficiency of iron can result in deficiency iron nature anaemia. An excess of iron can result in tissue inflammation, the multi-organs damnification and fibrosis pathological changes [1]. Iron goes into the body by food chain. After it is absorbed by human body, iron participates in various metabolism in human body. In general, the iron content in food is low and thus the development of a high sensitive method for the determination of iron is of interest.

The reported methods for the determination of iron deal with atomic absorption spectrometry [2, 3], fluorescent method [4], ICP (inductively coupled plasma)-MS (mass spectrometry) [5, 6], neutron activation analysis [7]. Unfortunately, these methods have the disadvantages that some instrumentation is expensive, operation can be complex, and they are difficult to be popularized. Catalytic kinetic spectrophotometry has the advantages that operation is simple and convenient and instrumentation is cheap, etc. Although some reports applying the kinetic method to the determination of iron have been proposed [8, 9], the selectivity of most of the methods are still poor. Thus, there is a demand for an inexpensive, simple and selective procedure to obtain more accurate information about iron levels in some samples such as food samples. *p*-Acetylarsenazo (ASApA, C₂₄H₁₉N₄O₁₂AsS₂) is an excellent chromogenic agent to be used for this type of analyses. The reagent has been used in the fading spectrophotometric determination of cerium(IV) [10]. This paper describes the catalytic effect of Fe(III) on the fading reaction of *p*-acetylarsenazo oxidized by potassium periodate in the sulfuric acid medium. Based on this principle, a novel catalytic kinetic spectrophotometric

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method for the determination of iron is developed. The present method has the advantages that sensitivity is high, operation is simple, analytical cost is low. It has been satisfactorily applied to the determination of trace iron in the food black gingili paste, oat slice, sleeve-fish silk.

EXPERIMENTAL

Apparatus. A 722S spectrophotometer (Shanghai Linggunag Technique Co., Ltd., China) with a 1.0 cm cell was used for measuring the absorbance. A HH-2 constant temperature water bath kettle (Jiangsu Jintan Ronghua Instrument Manufacture Co., Ltd, China) was employed to control the reaction temperature. For comparison analyses a Hitachi Z-8000 polarization Zeeman atomic absorption spectrophotometer was used to determine the iron content in the samples.

Reagents. Fe(III) standard solution: 0.0863 g of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (Shenyang First Plant for Reagent, China) was dissolved in 0.10 M sulfuric acid solution and diluted with 0.10 M sulfuric acid solution to 100 mL to give 1.79×10^{-3} M of iron(III) stock solution. When required, the stock solution was gradually diluted to 10 ng/mL (1.79×10^{-7} M); *p*-Acetylarsenazo (ASApA, Shanghai Changke Research Institute for Reagent, Jingsheng Chemical Limited Company, China) solution: 7.2×10^{-5} M. 0.0500 g of ASApA was dissolved a suitable amount of water and then diluted with water to 100 mL; KIO_4 (Chemical Reagent Company, Ltd, National Medicine Group, China) solution: 5.0×10^{-3} M. 0.1150 g of KIO_4 was weighed and dissolved in 100 mL of water; H_2SO_4 (Beijing Chemical Plant, China): 0.10 M. Unless specially stated, all reagents used in the experiments were of analytical reagent. The water used was deionised distilled water.

Procedure for iron. A sample solution was prepared by adding a suitable amount of the standard iron(III) solution (for variable optimization conditional experiments: 30 ng), into a 10 mL comparison tube. Then, 1.0 mL of 7.2×10^{-5} M ASApA solution, 0.8 mL of a 0.10 M H_2SO_4 solution and 1.0 mL of a 5.0×10^{-3} M KIO_4 solution were added. The solution was diluted to the mark with water, shaken well and placed into a boiling water bath at 100 °C heated for 7 min. The comparison tube was rapidly taken out, and cooled for 10 min in running water to terminate the reaction. The absorbance (catalytic reaction), A, was measured at 540 nm against water using 1 cm cells. The measurement of non-catalytic reaction absorbance, A_0 , was carried out in the absence of Fe(III). The net analytical signal was obtained from the difference of absorbance (ΔA) between the non-catalytic reaction (A_0) and the catalytic reaction (A), $\Delta A = A_0 - A$.

Procedure for the determination of iron in black gingili paste, oat slice, and sleeve-fish silk. About 5 g of black gingili paste, oat slice or sleeve-fish silk was weighed, respectively, and placed in a ceramic crucible. The samples were heated in an electrical oven until no more smoke was emitted. The sample was carbonized, placed in a muffle oven, and calcined for 24 h by increasing the temperature from a room temperature to 680 °C. It was taken out and cooled to room temperature. 4 mL of hydrochloric acid (1:1, v/v) and 2 mL of concentrated nitric acid were added to the ash component. The content was gently heated for dissolution and evaporated to near dryness. A small amount of water was added to the content. The solution was transferred to a 100 mL volumetric flask, diluted with water to the constant volume and shaken. 2.00 mL of the above test solution was taken out, placed in a 100 mL volumetric flask, diluted to the constant volume, shaken. 2.00 mL of the above test solution was taken out and placed in a 10 mL comparison tube for the determination of iron content by following the general procedure under the established optimum conditions. At the same time, the experiments of standard addition recovery were carried on for the determination of recovery according to standard

addition method. The recovery test was carried on according to the following procedure. Into the one 10 mL comparison tube were successively added 2.00 mL of the test solution, 30 ng of standard Fe(III) solution, 1.0 mL of 7.2×10^{-5} M ASApA solution, 0.8 mL of a 0.10 M H₂SO₄ solution and 1.0 mL of a 5.0×10^{-3} M KIO₄ solution, while in the other solution, the test solution and the standard Fe(III) solution were not put in the mixture. The determination of iron was carried out according to the procedure described. The total amount of iron was calculated based on the linear regression equation. The total amount, which was obtained from the above-calculation, subtracts the amount in the testing solution to obtain the amount of the recovered iron. This value was divided by the added amount of iron to obtain the recovery. Atomic absorption spectrometry was used to determine iron content in the above sample for comparison.

RESULTS AND DISCUSSION

Absorption spectra. The absorption spectra of ASApA solution, ASApA-KIO₄ system, ASApA-KIO₄-Fe(III) system against water were recorded (Figure 1) according to the proposed procedure. From the curves A and B it can be seen that the addition of KIO₄ resulted in the decrease in the absorbance of ASApA. This indicates that KIO₄ has an oxidation effect on the ASApA solution. A comparison of curve B with curve C and D showed that iron(III) has a catalytic effect on the ASApA-KIO₄ system. Curves C and D showed that with the increase in the amount of iron(III) the catalytic effect further increased. Over a definite amount of concentration, the addition amount of Fe(III) and ΔA present a linear relationship. This is the quantitative base for the determination of iron in this paper. The maximum absorption wavelengths of the catalytic reaction solution and the non-catalytic reaction systems are located at 540 nm. Moreover, the maximum absorbance difference of the two systems, ΔA , is at 540 nm. Therefore, 540 nm was selected as the measurement wavelength.

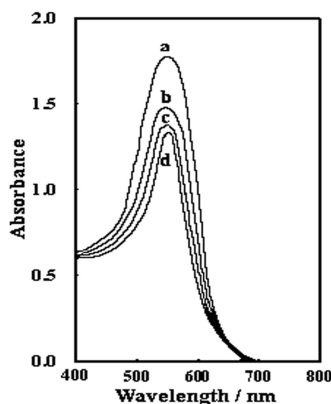


Figure 1. Absorption spectra. (a) ASApA (against water), (b) ASApA-KIO₄ (against water), (c) ASApA-KIO₄ + 15 ng Fe(III) (against reagent blank), (d) ASApA-KIO₄ + 30 ng Fe(III) (against reagent blank). [ASApA] = 7.2×10^{-6} M; [KIO₄] = 5.0×10^{-4} M; [H₂SO₄] = 8.0×10^{-3} M; heating temperature: T = 100 °C; heating time: t = 7 min.

Effect of acidity. Under the optimum conditions, the effect of the amount of 0.2, 0.5, 0.6, 0.8, 0.9, and 1.0 mL of 0.10 M sulfuric acid was added, respectively. The results showed as the amount of sulfuric acid increased under the test conditions, ΔA increased over the range of 0.2-0.8 mL. At 0.8 mL, ΔA was at maximum and the reaction sensitivity was at maximum. When

the volume of sulfuric acid solution was more than 0.8 mL, the reaction sensitivity decreased. Thus, 0.8 mL of 0.10 M sulfuric acid solution was selected for the control of acidity of the system. At this time the acidity of the system was 8.0×10^{-3} M.

Effect of the amount of ASApA. Under the optimum conditions, the effect of the amount of ASApA was studied. 0, 0.2, 0.5, 0.8, 1.0, 1.1, 1.2, 1.5 mL of 7.2×10^{-5} M ASApA solution was added, respectively. The results showed as the amount of ASApA increased under the test conditions, ΔA increased over the range of 0-0.8 mL. Over the range 0.8-1.1 mL, ΔA was a maximum. After 1.1 mL, ΔA decreased. Thus, 1.0 mL of 7.2×10^{-5} M ASApA solution was selected.

Effect of the amount of KIO₄. Under the optimum conditions, the effect of the amount of KIO₄ was studied. 0, 0.1, 0.2, 0.5, 0.8, 1.0, 1.2 and 1.5 mL of 5.0×10^{-3} M KIO₄ solution was added, respectively. The results showed as the amount of KIO₄ increased over the range 0-0.5 mL under the test conditions, ΔA increased. Over the range 0.5-1.5 mL, ΔA was a maximum and smooth. Therefore, 1.0 mL of 5.0×10^{-3} M KIO₄ solution was adopted.

Effect of heating temperature. Under the optimum conditions, experiments to determine the effect of reaction temperature were carried out. A water bath of 65, 70, 80, 85, 90, 95 and 100 °C, respectively, was used for heating. The results showed that as the reaction temperature increased under the test conditions, the reaction sensitivity increased. When the temperature of water bath reached 100 °C, ΔA was at maximum and reaction sensitivity was at maximum. Therefore, the water bath of 100 °C was selected and the system was cooled down by running water to terminate the reaction. The data obtained over 65-100 °C was regressed to obtain a linear regression equation: $\log A_0/A = -198.472/T (K) + 0.5824$, with a correlation coefficient $\gamma = 0.9916$. The activation energy of the catalytic reaction obtained according to the slope of the equation was $E_a = 89.99$ kJ/mol.

Effect of heating time. Under the optimum conditions, the experiments to determine the effect of heating time were carried out. The reaction system was heated for 0, 1, 3, 4, 5, 6, 6.5, 7, 7.5, 8 and 9 min, respectively. The results showed that a linear relationship was presented between ΔA and the heating time over 1-7 min. And at 7 min, ΔA was at maximum. After 7 min, ΔA gradually decreased. Thus, heating time was selected to be 7 min. A plot was drawn with ΔA to t and its linear regression equation was $\Delta A = 0.025 t (\text{min}) - 0.005$, with a correlation coefficient $\gamma = 0.9942$. The rate constant of the reaction calculated was $3.11 \times 10^{-4} \text{ s}^{-1}$. The half-life period was 3.709 min.

Stability of system. For the determination of 3.0 ng/mL Fe(III) a variation of ΔA of the reaction systems did not exceed $\pm 5\%$ within 3 h and stable time of the system was 3 h.

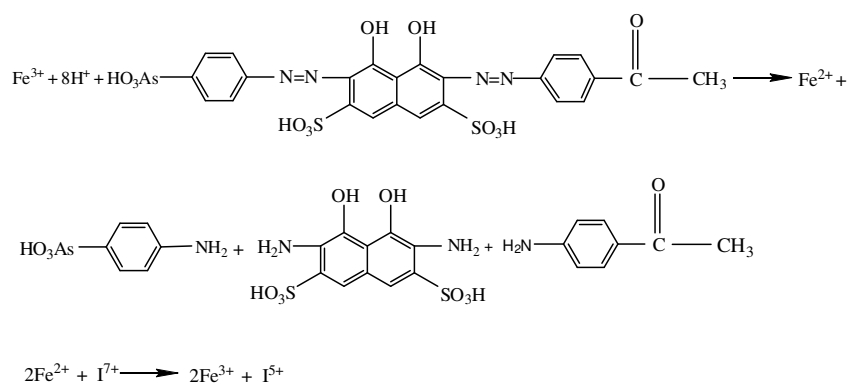
Effect of coexisting ions. Under the optimum experimental conditions the experiments to determine the effect of coexisting ions were carried out. When the determination of 3.0 ng/mL of Fe(III) was made and a relative error was controlled with $\pm 5\%$, the allowable amounts of coexisting ions (in mass multiple, m/m) are as follow: Ca²⁺, Mg²⁺, CH₃COO⁻ (100); Cd²⁺, Zn²⁺, B(III) (20); Pb²⁺, Al³⁺ (15); Bi³⁺, I⁻, F⁻, Br⁻ (10); Ag⁺, Cu²⁺ (5); Mn²⁺, Ni²⁺ (3); Ti(IV), W(VI), Mo(VI) (2); MnO₄⁻ (1); La³⁺ (0.6); Ce (IV), VO₃⁻ (0.5); Cr³⁺, Eu³⁺, Y³⁺, Th(IV) (0.2); Cr(VI) (0.1).

Calibration curve. Under the optimum conditions, the experiments to determine a linear range were carried out. The standard solution containing 0, 1.0, 2.5, 5.0, 10, 20, 25, 30, 35, and 40 ng

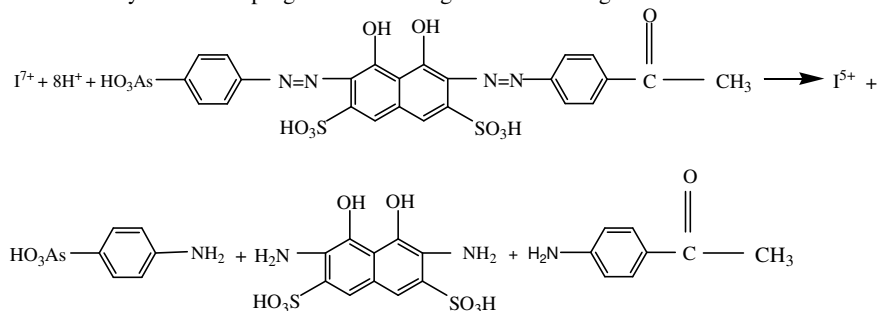
of Fe(III) was added, respectively. The results showed that under the optimum conditions a good linear relationship was presented over the range of 0.10-4.0 ng/mL for iron(III). Its regression equation was: $\Delta A = 4.91 \times 10^{-2} C$ (C: ng/mL) + 0.017, with a correlation coefficient $\gamma = 0.9966$. For thirteen replicate determinations of 3.0 ng/mL iron (III), the relative standard deviation of the method calculated was 3.12%. From 3 S/K method (S is the standard deviation of 11 replicate determinations of a blank solution, K is the slope of the regression equation) the detection limit of the method was calculated to be 0.031 ng/mL.

Mechanism of reaction. In the present paper, ASA_pA was used as the chromogenic agent, KIO₄ as the oxidant, Fe(III) as the catalyst. Based on the principle of catalytic reaction [11], the reaction mechanisms proposed are as follows:

The catalytic reaction progresses according to the following formula:



The non-catalytic reaction progresses according to the following formula:



Application

The present method was satisfactorily applied to determine the iron content in black gingili paste, oat slice and sleeve-fish silk samples. Table 1 summarizes the results, which are close to those obtained by atomic absorption spectrometry. The relative standard deviation of eleven replicated determinations of the present procedure was 1.34-1.78 %. The recovery of the method was 95.71-103.3 %. The analytical results of the method were quite satisfactory.

Table 1. Determination of iron in real samples.

Sample ^a	Found ($\mu\text{g/g}$)	Average ($\mu\text{g/g}$)	RSD (%)	Added (ng/g)	Recovered (ng/g)	Recovery (%)	Atomic absorption spectrometry ($\mu\text{g/g}$)
Black gingili paste	19.23, 19.64, 19.84, 19.03, 19.43, 19.43, 18.83, 19.03, 19.23, 19.43, 19.31	19.31	1.57	3.000	2.950	98.33	19.30
Oat slice	26.92, 27.13, 27.73, 26.92, 26.72, 27.93, 26.72, 27.13, 27.73, 27.53, 27.25	27.25	1.34	3.000	3.100	103.3	27.27
Sleeve-fish silk	34.41, 34.62, 35.22, 34.01, 34.21, 34.21, 35.22, 34.01, 34.82, 35.02, 34.58	34.58	1.78	3.500	3.350	95.71	34.58

^aBlack gingili paste, oat slice: product of Guangxi South Company, P.R. China; sleeve-fish silk: product of Dalian Aquatic Product Company, P.R. China.

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